PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Permeable Foamed Macromolecular Material

We, BAKELITE XYLONITE LIMITED, a British Company, of 27 Blandford Street, London, W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a fluid-permeable foamed macromolecular material, a process for its manufacture, and its use as a filter element.

It is known that certain materials having an open cell or sponge-like structure may be used as filtration media. Such materials will be permeable to particles of less than a specified size, and impermeable to particles of a greater size than this. Particles of a size theoretically able to pass through the material may be trapped within the material by repeated collision with the walls of the cells, or by reacting with the material, or with a coating applied to the walls of the cells of the material. Such reaction may be physical, for example, by absorption or adsorption in or on the walls, or chemical, by forming with the material or coating a compound of which the molecules will not pass through the material.

Materials having an open cell structure are thus suitable for use as filters, for example, for removing specific constituents from a fluid mixture or removing suspended particles from a fluid.

Such materials have been proposed as constituents of a filter-tip for a cigarette to extract certain constituents (thought to be harmful to health) from tobacco smoke entering the user's mouth.

[*Price* 4*s*. 6*d*.]

The present invention provides a process for the manufacture of a fluid-permeable shaped structure which comprises extruding a cell-forming expandable macromolecular material through an extrusion die so that it expands on emergence from the die, stretching the material by withdrawing it under tension from the die in such manner that the cells in the material are elongated and interconnected in the direction parallel to the applied tension to provide passages extending longitudinally through the structure alongside each other, and cooling the material whilst maintaining it in a stretched state.

The material should be withdrawn from the die under a tension such that its cross-sectional area in a plane perpendicular to the direction of extrusion is at most one quarter of the area which would have resulted from extrusion without stretching. The fraction to which the area has been reduced by stretching may be determined by measurement of the cross-sectional areas of stretched and unstretched rods of material after cooling to room temperature.

The material is preferably stretched to an extent such that its cross-sectional area in a plane perpendicular to the direction of extrusion is at most one ninth of the area which it would have if extrusion were carried out without stretching but under otherwise identical conditions.

The present invention also provides fluid-permeable shaped structures made by the process, and filter tip cigarettes prepared from shaped structures made by the process.

The longitudinal permeability of the shaped structure, that is the fluid permeability in a

direction parallel to the direction of the applied tension, may be increased by the formation of a number of additional continuous passages or channels in the structure, the channels being orientated substantially parallel to the direction of extrusion. Such channels may be produced, for example, by the presence of one or more gauzes in the extruder at a point close to the die orifice, the plane of each gauze being substantially perpendicular to the direction of extrusion. Each gauze is preferably constructed of metal wire, and is preferably of such dimensions that the number of channels thus produced in the shaped structure, which will correspond generally to the number of intersections of the elements of the gauze, is small compared with the number of elongated cells produced by the foaming agent (the numbers being counted in a plane perpendicular to the extrusion direction), while the cross-sectional area of the channels produced by the gauze will be large compared with the cross-sectional area of the elongated cells. The gauze dimensions may be, for example, of 20—100 mesh (British Standard 481—933), while the elongated cells may have a diameter, measured transversely to the direction of elongation, between, for example, 0.0005 and 0.05 cm.

The material is advantageously maintained in its stretched position during cooling by withdrawing it under tension from the die orifice at a rate which gives the desired degree of extension.

The shaped structure is preferably withdrawn from the die through a smooth bore sleeve positioned coaxially with, and a short distance from, the orifice. The sleeve may be of, for example, metal, and maintained at a temperature which will cool the shaped structure to a rigid state, thus "setting in" the degree of stretch, whilst giving it a uniform cross-section and improved smoothness to its surface. The end of the sleeve facing the orifice may be of a larger cross-section area than the remainder of the length of the sleeve, especially the central portion, which is advantageously of a uniform cross-section of the same shape as, but slightly less in area than, that of the shaped structure as it enters the sleeve. The shaped structure is advantageously a rod of circular cross-section, and the central portion of the sleeve is preferably of slightly smaller diameter than the diameter of the rod as it enters the sleeve. There may be provided a plurality of sleeves, if desired maintained at differing temperatures. The or each sleeve may be maintained at a suitable temperature by, for example, water or air cooling.

A film of liquid or gas may be maintained between the surface of the shaped structure and the internal surface of the or each sleeve, to lubricate the structure as it passes through the sleeve. The pressure in the region between the die orifice and the end of the sleeve nearer to it may be maintained at a pressure other than atmospheric, either above or below atmospheric.

Longitudinal permeability may be further increased, if desired, by gently rolling the shaped structure between plates or rollers or subjecting it to gentle crushing in several directions perpendicular to the direction of elongation of the interconnected cells.

The longitudinal permeability of the shaped structure is preferably such that the rate of flow of air through one square centimetre of the material parallel to the direction of the pressure gradient exceeds 100 cubic centimetres per minute when the pressure gradient is 10 centimetres of water per centimetre.

Macromolecular materials suitable for use in the present invention are, for example, polystyrene, a copolymer of styrene with vinyl toluene, methyl methacrylate, acrylonitrile, or other acrylates or methacrylates, polyethylene, polyvinyl acetate, polyvinyl chloride, a copolymer of vinyl chloride and vinyl acetate, a graft copolymer of styrene on a polyvinyl chloride trunk, a graft copolymer of vinyl chloride on a polystyrene trunk, polyvinylidene chloride, and post-chlorinated polyvinyl chloride, foamed by incorporating therein a suitable blowing agent, among which may be mentioned, for example, pentane, hexane and/or other hydrocarbons boiling below the normal softening temperature of the relevant polymer, gases injected under pressure into the extruder (for example, carbon dioxide, nitrogen or helium), materials which decompose under the extruding conditions to give a gas, for example azodicarbonamide, mixtures of such blowing agents, if desired in combination with substances which assist "even blowing" to give cells of constant, small, size, for example, finely dispersed liquid water, sodium bicarbonate and citric acid (added successively), or other carbon dioxide-forming mixtures (i.e. a mixture of a preferably solid acid and a carbonate).

As an example of a suitable combination of such materials there may be mentioned polystyrene to which has been added 6% *n*-hexane, 1% citric acid and 1% sodium bicarbonate (the percentages being by weight, based on the weight of polystyrene).

The material is preferably extruded as a rod of circular cross-section, advantageously of such diameter that when stretched by an amount sufficient to elongate and connect the cells according to the invention its diameter is that of the cigarette into which it is desired to insert the material. Such rods may then be divided into suitable lengths for incorporation into cigarettes.

After stretching, the structure may be contacted with, for example, immersed in the liquid (e.g. a solution) or vapour of one or more suitable sequestering, chelating, or other

complex-forming agents, which will react selectively with undesired components of the fluid to be filtered. Alternatively such complexing agents may be added to the monomer before polymerization, or to the polymer before blowing.

For example poly(ethylene oxide) having a molecular weight between 1,000 and 1,000,000 may be added to a polymer, for example, polystyrene, before blowing. The stretched rod then acts as a selective filter for phenol.

Other materials which may be added are, for example, cellulose acetate, polyvinyl acetate, polyvinyl amine, poly(2,2-diaminomethyloxypropylene) poly(propylene oxide), surface active agents, plasticisers, and inorganic materials, for example, china clay, activated charcoal, infusorial earth vermiculite, natural or synthetic zeolites, or two or more of such substances.

The following Examples illustrate the invention:

Example 1

A polystyrene resin, of intrinsic viscosity (or limiting viscosity number) of 0.75 measured in toluene solution at 25°C, in which 5% by weight of a light petroleum fraction (boiling range 30—40°C) was incorporated during polymerization was pre-extruded with 0.8% by weight citric acid, as 1/8 in. diameter rods. These rods were water cooled immediately on emergence from the extrusion die to prevent expansion and chopped up to produce extrusion pellets. The pellets were tumbled with a small quantity of liquid paraffin and 0.9% by weight sodium bicarbonate.

The coated pellets were fed into the hopper of a 1.25 in. twin screw laboratory extruder fitted with a 0.25 in. diameter extrusion nozzle. A grid, backed by a gauze pack (20 mesh, 120 mesh, 20 mesh.) (British Standard) was placed in the coupling piece between the barrel and the extrusion nozzle. The feed hopper was water cooled to maintain it at 70°C, the front part of the barrel being maintained at 140°C and the nozzle at 160°C. The speed of the screw was 10 rpm and the extrusion rate 5 lb. per hour. The rod which emerged from the nozzle expanded within a short distance from the die to approximately 0.75 in. in diameter.

The rod was stretched from the die and fed through a smooth bore water-cooled tube of copper to act as a sizing and cooling sleeve. The bore of the sleeve was 5/16 in. and the bell mouthed entrance was held ½ in. from the extrusion nozzle. The rod was withdrawn continuously from the sleeve at a uniform linear rate of 20 feet per minute, to produce a rod of density 0.12 gram/cc.

The stretched rod was permeable to the passage of air along its length, the mean resistance to flow being 10 cm of water gauge per cm length for an air flow rate of 1000 cc/minute. The mean diameter of the longitudinal channels was approximately 0.017 cm.

Example 2

The procedure of Example 1 was followed with the exception that 10% by weight of finely ground activated charcoal was added to the pellets immediately before extrusion as rod. A smooth longitudinally permeable rod was obtained, the cell size being similar to that obtained by the procedure of Example 1. Examination under the microscope showed that particles of activated charcoal protruded from the walls of the cells.

Example 3

The procedure of Example 1 was followed, with the addition of 5% of a polyethylene oxide polymer (Union Carbide WSR 35) to the pellets before extrusion, to give increased retention of phenol.

Example 4

A wire mesh gauze was fixed at the exit of the die nozzle normal to the stream of plastic. The procedure of Example 1 was otherwise followed. The resulting rod of expanded polystyrene was found to have a series of larger continuous holes running lengthwise corresponding in number and position to the points of intersection of the gauze wires, and was highly permeable to the flow of gases along its length.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a fluid-permeable shaped structure which comprises extruding a cell-forming expandable macromolecular material through an extrusion die so that it expands on emergence from the die, stretching the material by withdrawing it under tension from the die in such manner that its cross-sectional area is reduced to at most one quarter of the area which would have resulted from extrusion without stretching to elongate the cells in the material and interconnect them in the direction parallel to the applied tension thereby providing side-by-side passages extending longitudinally through the structure, and cooling the material whilst maintaining it in a stretched state.

2. A process as claimed in claim 1, wherein the macromolecular material is stretched as it is withdrawn from the die to an extent such that its cross-sectional area is reduced to at most one ninth of that which it would have if extruded without stretching.

3. A process as claimed in any one of claims 1 to 2, wherein a number of continuous passages or channels are formed in the shaped structure in addition to those resulting from the interconnexion of the cells.

4. A process as claimed in claim 3, wherein the continuous passages or channels are

formed by a gauze in the extruder close to the die orifice.

5. A process as claimed in any one of claims 1 to 4, wherein the shaped structure is withdrawn from the die through a smooth bore sleeve coaxial with the orifice and spaced apart therefrom.

6. A process as claimed in claim 5, wherein the end of the sleeve nearer to the orifice is of a larger diameter than the central portion of the sleeve, the central portion being of the same shape as, but of slightly smaller area than, the shaped structure as it enters the sleeve.

7. A process as claimed in claim 5 or claim 6, wherein there is provided a plurality of sleeves, each maintained at different temperatures.

8. A process as claimed in any one of claims 5 to 7, wherein there is maintained between the surface of the shaped structure and the internal surface of the or each sleeve a film of liquid or gas.

9. A process as claimed in any one of claims 1 to 8, wherein the shaped structure is rolled between plates or rollers or subjected to crushing in directions perpendicular to the direction of elongation of the interconnected cells.

10. A process as claimed in any one of claims 1 to 9, wherein the cell-forming expandable macromolecular material is any one of the macromolecular materials hereinbefore specified.

11. A process as claimed in any one of claims 1 to 10, wherein the shaped structure is of circular cross-section.

12. A process as claimed in any one of claims 1 to 11, wherein the stretched shaped structure is contacted with the liquid or vapour of a sequestering, chelating or other complexing agent.

13. A process as claimed in any one of claims 1 to 11, wherein the cell-forming expandable material or the monomer from which it is derived is contacted with a chelating, sequestering or other complexing agent before being extruded.

14. A process as claimed in claim 1, conducted substantially as described in any one of the Examples herein.

15. A fluid-permeable shaped structure whenever produced by a process as claimed in any one of claims 1 to 14.

16. A fluid-permeable shaped structure as claimed in claim 15, wherein the longitudinal permeability is such that the rate of flow of air through one square centimetre of the material parallel to the direction of the pressure gradient exceeds 100 cubic centimetres per minutes when the pressure gradient is 10 centimetres of water per centimetre.

17. A cigarette filter, whenever prepared from a structure as claimed in claim 15 or claim 16.

18. A cigarette containing a filter as claimed in claim 17.

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